

DETERMINATION OF SULFUR AS BARIUM SULFATE IN THE PRESENCE OF FERRIC IRON

by

OSCAR MILNER AND WALLACE M. McNABB

Department of Chemistry and Chemical Engineering, University of Pennsylvania, Philadelphia, Penna (U.S.A.)

Considerable interest still exists in the determination of sulfur as barium sulfate in the presence of iron. The most recent work is that of WALDBAUER, ROLF, AND FREDIANI⁴, who carried out a spectrographic study of the coprecipitation of the fourth period elements with barium sulfate. They state that the contamination of the precipitate with iron may possibly be due to the formation of a complex ion containing iron in the form of "ferric sulfuric acid."

KUSTER AND THIEL³ precipitated the iron as ferric hydroxide, then precipitated the sulfate as barium sulfate in the ammoniacal solution, and dissolved the ferric hydroxide with hydrochloric acid prior to filtering the barium sulfate. BRADDOCK-ROGERS¹ applied this method, with some modifications, to the determination of sulfur in pyrite. Good results are reported in the presence of small amounts of iron.

The object of this investigation was to find the best conditions to eliminate the coprecipitation of ferric iron in the precipitation of sulfur as barium sulfate by the method of KUSTER AND THIEL³. In order to give the method a fair test it was necessary to carry out the precipitations in solutions as free as possible of foreign ions.

All chemicals were C.P. reagent grade.

EXPERIMENTAL

Standard solutions of sulfuric acid of approximately the desired strength were prepared and analyzed according to the method of HILLEBRAND AND LUNDELL². Four determinations carried out by the procedure recommended by KUSTER AND THIEL³ gave an average percentage error of -0.73. The precipitates were found to be contaminated with iron.

A number of analyses were made according to the method of BRADDOCK-ROGERS¹. A relatively complete separation of iron was obtained when present in quantities less than 50 mg; however, the results for sulfur were slightly high,

References p. 388.

apparently because of the occlusion of barium chloride. Therefore, the strength of the barium chloride was reduced from 10 to 5 per cent, and the solution added more slowly. The amount of ferric hydroxide retained in the precipitate of barium sulfate decreased with a decrease in the rate of addition of the barium chloride. The optimum rate was found to be 1 to 1.5 ml per minute. It was noted that if the ammoniacal solution was boiled, the coagulated ferric hydroxide would not dissolve completely upon subsequent acidification. Care was exercised to keep the solution just below the boiling point while adding the barium chloride.

The effect of allowing the barium sulfate to crystallize in the ammoniacal solution before adding the acid was investigated to determine whether contamination could be decreased. The precipitate under these conditions became almost brick-red in color, whereas immediate addition of the acid gave a light pink precipitate which was easily purified by washing with a 1 per cent hydrochloric acid solution after decantation, permitted a decreased number of final washings, thus minimizing the loss of barium sulfate through solubility.

PROCEDURE

Solutions of sulfuric acid and ferric chloride were transferred to a 400-ml beaker and diluted to a volume of 200 ml with distilled water. To this were added 5 ml of ammonium hydroxide (specific gravity 0.90) and the solution was heated almost to boiling. A 5-ml excess of warm 5 per cent barium chloride solution was added dropwise at the rate of 1 to 1.5 ml per minute to the warm solution with continuous stirring. The solution was neutralized with concentrated hydrochloric acid and an excess of 1 per cent by volume added. After heating and stirring until the ferric hydroxide had completely dissolved, the beaker was placed on a steam bath for 3 hours. The solution was allowed to cool to room temperature and carefully, without disturbing the precipitate, decanted through a No. 42 or No. 44 Whatman filter paper. The paper was washed with acidulated hot water (2 ml of concentrated hydrochloric acid to 1 litre of distilled water) until 10 ml gave a negative test for iron with thiocyanate. Placing the beaker obliquely across the top of a beaker of the same size was found to facilitate the decantation. The precipitate remaining in the beaker was moistened with 1 ml of concentrated hydrochloric acid. The sides of the beaker were washed down with 5 ml of hot water and the beaker was placed on the steam bath for several minutes. The solution was diluted with boiling water and digested on a hot plate for 20 to 30 minutes, the volume being kept at about 100 ml.

The solution was allowed to cool to room temperature and filtered through the original paper. The precipitate was washed four times with 5-ml portions of acidulated hot water and finally washed free of chlorides. The paper containing the precipitate was charred and burned the usual way, the barium sulfate ignited at 750° to 800° C and weighed.

References p. 388.

DISCUSSION

A procedure is recommended for the determination of sulfur as barium sulfate in the presence of ferric iron which has been tested up to a concentration of 200 mg of iron. Twenty-five determinations, carried out with concentrations of 100 to 300 mg of sulfuric acid in the presence of 20 to 200 mg of iron, gave a maximum deviation of +0.39 to -0.33 in percentage error. The ignited barium sulfates were white, and colorimetric determinations of iron from the decomposed precipitates showed no more than 0.1 to 0.3 mg in any case. Iron present in quantities greater than 200 mg gave contamination which could not be removed completely.

SUMMARY

A procedure is recommended for the determination of sulfur as barium sulfate in the presence of ferric iron.

Iron present in quantities greater than 200 mg gives contamination.

RÉSUMÉ

Les auteurs décrivent une méthode, permettant de doser le soufre à l'état de sulfate de baryum, en présence d'ions ferriques.

Le fer (III) gêne en quantités supérieures à 200 mg.

ZUSAMMENFASSUNG

Eine Methode zur Bestimmung von Schwefel als $BaSO_4$ in Gegenwart von Fe (III)-Ionen wurde beschrieben.

Dreiwertiges Eisen stört in Mengen von mehr als 200 mg.

REFERENCES

- ¹ K. BRADDOCK-ROGERS, *Action of Air-Carbon Tetrachloride Vapor Mixtures on Certain Natural and Artificial Sulfides and on Selenides and a Telluride*. Dissertation, University of Pennsylvania, 1928.
- ² HILLEBRAND AND LUNDELL, "*Applied Inorganic Analysis*". John Wiley & Sons, New York 1929, p. 578.
- ³ KUSTER AND THIEL, *Z. anorg. Chem.*, 22 (1900) 424.
- ⁴ WALDBAUER, ROLF, AND FREDIANI, *Ind. Eng. Chem., Anal. Ed.*, 13 (1941) 888.

Received January 13th 1950